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Polarographic Reduction of Carbon Dioxide and Its Sulfur Derivatives in Non-Aqueous Solvents

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The polarographic reduction of CO_2, COS, and CS_2 has been studied in several aprotic solvents and in DMF-water mixtures. COS gives one wave in most solvents, presumably by one-electron step, at less negative potential than the wave of CO_2 and at more negative than the first wave of CS_2, as expected.

A week proton-donor, such as water or phenol affects on the second wave of CS_2, while benzoic acid on even the first wave in DMF. By the use of a higher alkyl-substituted tetraalkylammonium ion as the supporting electrolyte, the second wave of CS_2 shifts to more negative potential. Good liniarity is found between the donor number of the solvent and the half-wave potential of the wave of CO_2 and COS, and of the first wave of CS_2.

INTRODUCTION

The electrochemical reduction of carbon dioxide is interesting from the theoretical aspect and also from the standpoint of carbon resource. It has been reported that carbon dioxide is reduced to oxalate,[1] or carbon monoxide and carbonate[2,3] in aprotic solvents. Carbon dioxide monoanion radical $CO_2^{\cdot-}$ ion is suggested to exist as an intermediate.[4] But little is known about the reduction mechanism in either water or aprotic solvents.[5] Carbon disulfide gives two polarographic waves at the dropping mercury electrode,[6] but one wave at the platinum electrode[7] in the aprotic solvent, and different mechanisms are discussed.

In the present paper, we report the polarographic behavior of carbon dioxide, carbon disulfide and carbonyl sulfide (COS) in several aprotic solvents. The half-wave potentials are considered in terms of the donor number of the solvent. The effects of proton donors and supporting electrolyte cation on the reduction of carbon disulfide were also investigated in detail.

EXPERIMENTAL

Solvents and Reagents

Commercially obtained acetonitrile (AN), propylen carbonate (PC), dimethylformamide (DMF), dimethylacetamide (DMA), dimethylsulfoxide (DMSO), and hexamethylphosphoramide (HMPA) were purified by the following procedure: AN was stirred for several days in contact with calcium hydride, which was decanted and then distilled twice over phosphorus pentoxide and over calcium hydride. PC was vacuum distilled twice, adding a small amount of p-toluensulfonic acid. DMF was purified by being vacuum distilled twice, after dried with calcium hydride. DMA

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was dried with calcium hydride, and vacuum distilled. In the second distillation, a small amount of p-toluensulfonic acid was added. DMSO was distilled twice under vacuum. HMPA was refluxed over calcium hydride and vacuum distilled twice with an adiabatic vacuum fractional distillation column made by Shibata Chemical Apparatus Mfg. Co., Ltd.

Carbon disulfide from Nakarai Chemicals, guaranteed reagent was distilled once and stocked in the dark. Carbon dioxide obtained from Takachiho Chemicals and calbonyl sulfide (COS) from Matheson Coleman & Bel were used without further purification. Perchlorates of lithium, sodium, potassium, rubidium, tetramethylammonium (Me_4N^+), tetraethylammonium (Et_4N^+), tetra-n-propylammonium (Pr_4N^+), teta-n-butylammonium (Bu_4N^+), and tetra-n-hexylammonium (Hex_4N^+) were prepared following the method of the previous reports.[8] Ammonium perchlorate (NH_4^+) was also prepared by the similar method.

Apparutas and Procedure

D.c. polarograms were recorded with a Yanagimoto three-electrode polarograph Model P8-DP and a.c. polarograms with Model P8-A. An H-type polarographic cell with a fine porosity sintered glass disk between the two compartments was used. The potentials were referred to an aqueous SCE or a silver-silver perchlorate electrode with each solvent (Ag/0.1 M $AgClO_4$, the solvents). The Ag/Ag^+ electrode with AN, PC, DMF, DMA, DMSO, and HMPA had a potential of +0.36 V, +0.78 V, +0.52 V, +0.45 V, +0.33 V, and +0.37 V, respectively against the aqueous SCE.

A platinum wire served as an auxiliary electrode. The dropping mercury electrode had the following characteristics in DMF-0.1 M Et_4NClO_4 at the mercury head of 60 cm: $m = 0.68$ mg/S with the open circuit, and $t = 3.2$ S at −2.1 V *vs.* Ag/Ag^+ electrode. All measurements were carried out at 25±0.2°C.

The sample solution of CO_2 or COS was prepared by adding a proper amount of saturated solution of CO_2 or COS into the previously deoxygenated solvent containing the supporting electrolyte. The concentration was estimated by the comparison of wave height with that of CS_2 of a known concentration.

RESULTS AND DISCUSSION

1 Polarography of CS_2 in DMF and DMF-Water Mixtures

1-1 Reduction of CS_2 in DMF

Carbon disulfide gives two waves in 0.1 M Et_4ClO_4-DMF solution (Fig. 1). The half-wave potentials are −2.06 V and −3.20 V *vs.* Ag/Ag^+ electrode (listed in Table III). A very small intermediate wave was observed at −2.6 V.

Figure 2 shows the effect of the concentration of the supporting electrolyte on the wave height. The height of the first wave is not affected. That of the second wave is decreased with decreasing concentration of the supporting electrolyte owing to the increasing of migration current. This result suggests that the first wave is due to the reduction of a neutral molecule and the second wave to the reduction of a negative-charged species.

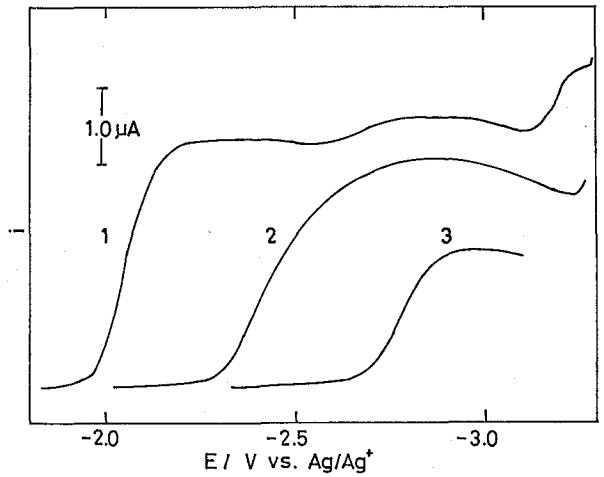

Fig. 1. D.c. polarograms of CS_2, COS, and CO_2 in DMF containing 0.1 M Et_4NClO_4. (1) 1.0 mM of CS_2, (2) about 1.0 mM of COS, (3) about 0.58 mM of CO_2.

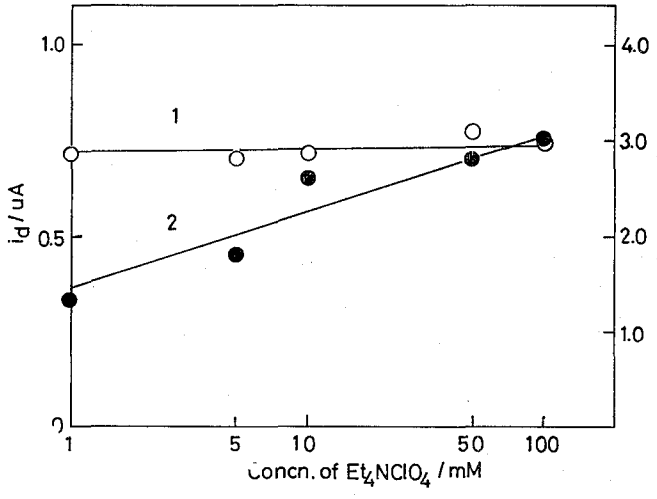

Fig. 2. Effect of concentration of the supporting electrolyte on the wave height of CS_2 in DMF. (1) the first wave, (2) the second wave. Concn. of CS_2 is fixed at 1.0 mM.

1-2 Reduction of CS_2 in DMF-Water Mixtures

In Fig. 3, d.c. polarograms of CS_2 in DMF-water mixtures are shown. The effect of water on the first wave is not remarkable. The second wave is sensitive to a small amount of water; the wave height increases and the half-wave potential shifts to less negative with the increase of water content. In 100 % water, CS_2 gives two waves of approximately same height which has been reported by Kolthoff *et al.*[9] The effect of water on the half-wave potentials is shown clearly in Fig. 4. A.c. polarograms are also measured in DMF-water mixtures, and values of $i_{ac}/i_{dc} \cdot t^{1/2}$ as a measure

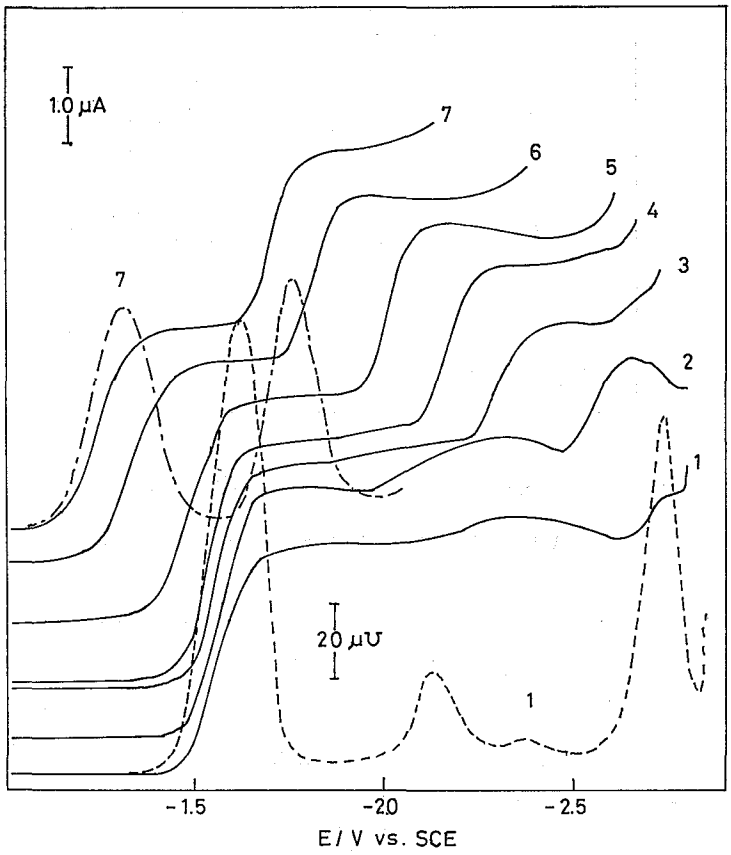

Fig. 3. CS_2 (1.0 mM) waves in DMF-water mixtures containing 0.1 M Et_4NClO. The solid lines; d.c. polarograms, the broken lines; a.c. polarograms. (1) water-free, (2) 2 %, (3) 10 %., (4) 20 %, (5) 35 %, (6) 70 %, (7) 100 % of water.

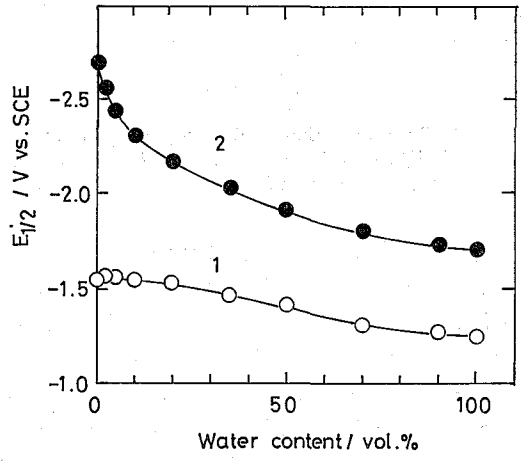

Fig. 4. Half-wave potentials of CS_2 in DMF-water mixtures. (1) the first wave, (2) the second wave.

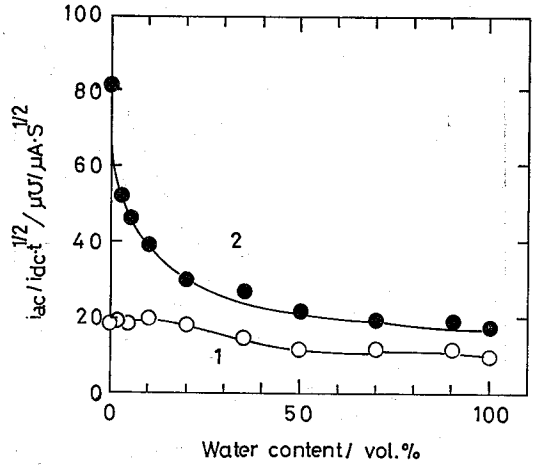

Fig. 5. $i_{ac}/i_{dc}\cdot t^{1/2}$ values for the waves of CS_2 in DMF-water mixtures. (1) the first wave, (2) the second wave.

of the reversibility[10,11] are shown in Fig. 5. The curves show that the second wave is fairly reversible in DMF, but becomes irreversible in aqueous solution.

Wawzonek *et al.*[6] found that CS_2 forms trimers in the electro-reduction in DMF. Seeber *et al.*[7] obtained the same product that Wawzonek did, although he proposed a quite different mechanism for the reduction of CS_2 in DMF. According to our polarographic results, the following reduction process is presumed. That is; at the first wave, anion radical $CS_2^{\cdot-}$ is formed, a small portion of which may slowly trimerize through the mechanism of Seeber or Wawzonek. At the second wave, the anion radical is further reduced to dianion CS_2^{2-}. Water added to DMF could suppress the trimerization of CS_2.

In order to examine whether the protonation of CS_2^{2-} occurs with the water molecule or with the proton produced by the dissociation of water, Et_4NOH was added[11] to decrease the activity of proton into the DMF solution containing 5 % to 90 % water. But the reduction waves promptly disappears because CS_2 reacts with DMF or impurity amines into the compound which is oxidized[12] at much more positive potential. Only at water content 100 %, the reduction wave is observed. Though a big increase in pH is expected due to hydroxyl ions, the wave is not influenced by the addition of Et_4NOH. From this results, the protonation reaction seems to occur between CS_2^{2-} ion and water molecule.

1-3 The Effect of Acids

The effect of phenol and benzoic acid was examined. Phenol affects largely on the second wave as shown in Fig. 6. By the addition of phenol, the height of the second wave increases and the half-wave potential shifts to positive potential. The second wave shows a nature of reaction current because the limiting current is not proportional to the square root of the height of mercury head.

Benzoic acid affects the first wave; the wave height increases by the addition of the acid and the half-wave potential shifts to positive potential. Therefore, it seems that the protonation occurs on $CS_2^{\cdot-}$ to produce CS_2H, which is reduced at the same

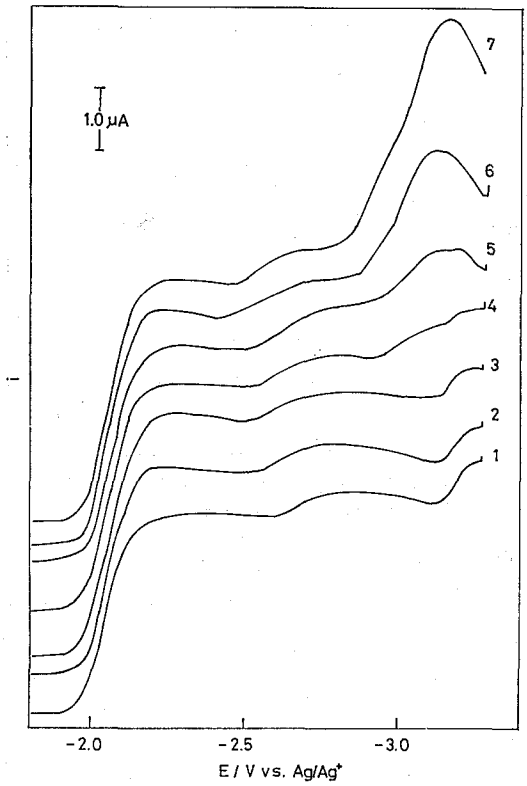

Fig. 6. Effect of phenol on CS_2 waves in DMF containing 0.1 M Et_4ClO_4. Concn. of phenol; (1) 0, (2) 2, (3) 3, (4), 4 (5) 5, (6) 7, (7) 10 mM.

potential as CS_2. The second wave is not well observed because benzoic acid is reduced at the less negative potential ($E_{1/2}=-2.56$ V) than the second wave of CS_2.

1-4 The Effect of the Cation of the Supporting Electrolyte

Various alkali metal perchlorates and tetraalkylammonium perchlorates were used as supporting electrolytes. The reduction waves of CS_2 in DMF containing various supporting electrolytes are shown in Fig. 7. When an alkali metal or ammonium perchlorate is used, the second wave is masked by the final rise of current. The wave height of the second wave becomes higher by the use of higher alkyl-substituted tetraalkylammonium ion. And the larger is the alkyl chain of supporting electrolyte, the less reversible becomes the first wave (Table I). The broken-line in Fig. 7 shows the a.c. polarograms with Me_4NClO_4 as supporting electrolyte. The first and the third peak correspond to the first and the second wave in d.c. polarograms. The second peak which appears clearly with Me_4N^+ as the supporting electrolyte, decreases with Et_4N^+ or Pr_4N^+, and disappears utterly with Hex_4N^+. This peak has a tensammetric nature, because the polymerization intermediate, as described in 1–2, is produced and absorbs on the electrode surface.

The half-wave potential in Table I is plotted against the crystal radius of supporting electrolyte cation (Fig. 8). The half-wave potential of the first wave is

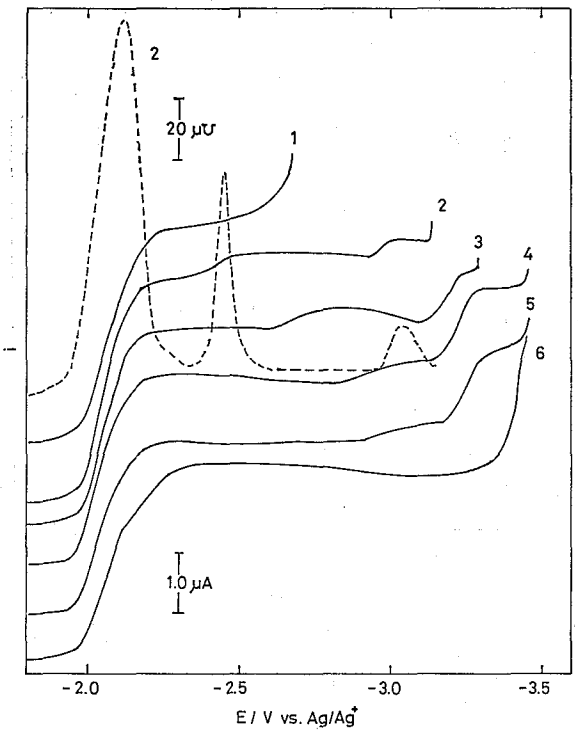

Fig. 7. The waves of CS_2 (1.0 mM) in DMF containing various supporting electrolytes. The solid lines; d.c. polarograms, the broken line; a.c. polarogram. The supporting electrolytes are, (1) Li^+ (2) Me_4N^+, (3) Et_4N^+, (4) Pr_4N^+, (5) Bu_4N^+, (6) Hex_4N^+.

Table I. Polarographic Data of CS_2 in DMF Containing Various Supporting Electrolytes at 25°C.

Supporting electrolyte cation	Ionic radius (A)	Half-wave potential		Slope	
		1st wave	2nd wave	1st wave	2nd wave
Li^+	0.60	−2.07	—	107	—
Na^+	0.95	−2.08	—	111	—
K^+	1.33	−2.10	—	110	—
NH_4^+	1.45	−2.00	—	59.3	—
Mc_4N^+	3.47	−2.06	-2.97_5	81.9	unmeasurable[a]
Et_4N^+	4.00	−2.06	−3.20	85.1	51.6
Pr_4N^+	4.52	−2.04	−3.23	73.0, 111[b]	56.5
Bu_4N^+	4.94	−2.05	−3.26	90.4, 107[b]	50.7
Hex_4N^+	5.6	−2.08	−3.42	90.7, 186[b]	unmeasurable[c]

Each supporting electrolyte is the form of perchlorate salt, and its concentration is 0.1 M. Half-wave potential; *vs.* Ag/Ag^+ electrode, solpe; mV. a) Unmeasurable owing to its small current. b) There is much difference of the slope between the front-half and the rear-half of the wave. c) The wave is too negative to measure the slope.

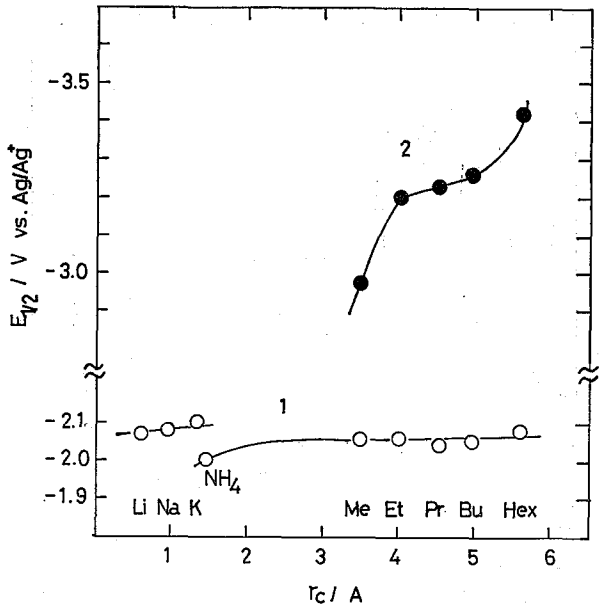

Fig. 8. The half-wave potential of CS_2 and ionic radius of the supporting electrolyte cation. (1) the first wave, (2) the second wave.

almost constant. As for the second wave, the half-wave potential shifts to more negatively with the order of $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Hex_4N^+$.

2 Polarography of CO_2 and COS in DMF and DMF-Water Mixtures

CO_2 and COS gives one wave in DFM solution containing 0.1 M Et_4ClO_4, while CS_2 gives two waves accompanied by the small intermediate wave. The reversibility of the waves of CO_2 and COS is low; the log-plot value of wave analysis is 86.4 mV and 159 mV, respectively (Fig. 1 and Table III). The half-wave potential of CO_2 is -2.79 V, and that of COS is -2.45 V *vs.* Ag/Ag^+ electrode. COS is reduced more easily than CO_2, but less than CS_2.

The half-wave potential of CO_2 shifts to positive potential and the reversibility decreases by the addition of water. At last apparent limiting current cannot be observed when the water content reaches 50 % by volume. As for COS, similar result is obtained (shown in Fig. 9). Therefore, COS is reduced to monoanion radical at the dropping mercury electrode as CO_2, and the radical may react slowly with water molecule.

3 The Relation between the Donor Number of the Solvent and the Half-Wave Potential

3-1 The Viscosity of the Solvent and the Diffusion Current Constant of CS_2

Polarographic reduction of CS_2 was carried out in various solvents. The limiting currents in these solvents are confirmed to be diffusion controlled by the linear proportionality of the limiting currents to the CS_2 concentration, and also to the square

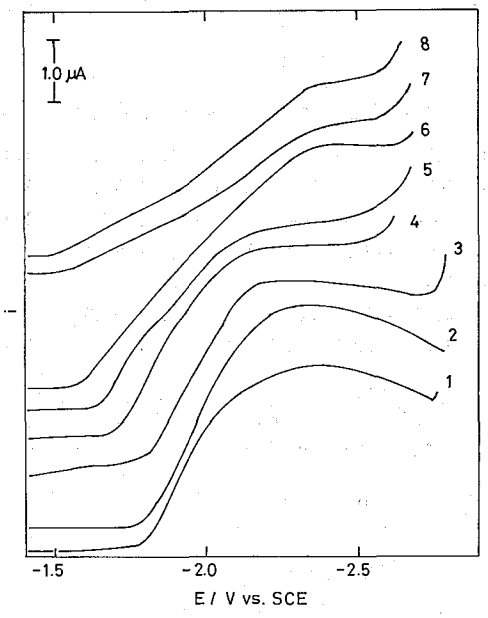

Fig. 9. COS waves in DMF-water mixtures containing 0.1 M Et_4NClO_4 at 25°C. Concn. of COS are about 1 mM. (1) water-free, (2) 2 %, (3) 10 %, (4) 35 %, (5) 50 %, (6) 70 %, (7) 90 %, (8) 100 % of water.

Table II. Diffusion Current Constant and Diffusion Coefficient of CS_2 and Viscosity of Solvent

Solvent	η, cp	I_1	I_2	D_1, cm^2/s	$I_1 \times \sqrt{\eta}$
AN	0.340	5.2_1	1.8_6	$7.3_6 \times 10^{-5}$	3.04
PC	2.53	3.4_0	1.8_4	3.1_5	5.41
H_2O	0.894	2.6_6	2.5_4	1.9_2	2.52
DMF	0.796	3.1_1	0.9_6	2.3_6	2.77
DMA	0.92	3.0_8	—[a]	2.5_8	2.95
DMSO	2.00	2.3_7	0.8_1	1.5_3	3.34
HMPA	3.47	1.5_0	1.0_8	0.6_1	2.79

η; viscosity of solvent at 25°C, I_1 and I_2; diffusion current constant of the first wave and the second wave ($uA \cdot mg^{-2/3} \cdot S \cdot mM^{-1}$), D_1; diffusion coefficient of the first wave. a); See b) in Table III.

root of the height of the mercury head. The relation between the viscocity (η) of solvent and the diffusion current constant (I) of CS_2 was examined, and the results are summerized in Table II. The value of $I \times \eta$ for the first wave is approximately constant, except in PC and water. The polarographic diffusion coefficients are calculated using the simple Ilkovic equation, and also summarized in Table II.

3-2 The Half-Wave Potential of CO_2, COS, and CS_2 in Various Solvents

The polarographic results of CO_2, COS, and CS_2 in all solvents of different donor number are shown in Table III. The concentration of CS_2 is kept constant, but those of CO_2 and COS are evaluated from the ratio of the wave height to the

Table III. Polarographic Data of CO_2, COS, and CS_2 in Various Solvent at 25°C.

Solvent		CO_2			COS			First wave		CS_2	Second wave		$RbClO_4$
	DN	$E_{1/2}$	Slope	Concn.	$E_{1/2}$	Slope	Concn.	$E_{1/2}$	Slope	Concn.	$E_{1/2}$	Slope	$E_{1/2}$
AN	14.1	−2.72	80.0	1.1	−2.45	204	0.79	−1.99	55.4	1.0	−3.00	41.4	−2.33
PC	15.1	−3.15	84.5	0.88	−2.83	146	0.66	−2.38	71.6	1.0	−3.34	62.0	−2.77
H_2O	18.0	—	—	—	—	—	—	−1.24[a]	94.3	1.0	−1.71[a]	59.0	−2.13[a]
DMF	26.6	−2.79	86.4	0.58	−2.45	159	1.0	−2.06	85.1	1.0	−3.20	45.0	−2.55
DMA	27.8	−2.74	89.9	1.0	−2.37	112	0.84	−2.00	84.9	1.0	−3.20[b]	—	−2.49
DMSO	29.8	−2.59	87.7	0.94	−2.22	129	1.1	−1.82	75.3	1.0	−2.93	55.9	−2.39
HMPA	38.8	−2.63	77.8	1.1	−2.25[c]	92.5	1.2	−1.86	96.0	1.0	−2.51	82.9	−2.38

Half-wave potential; *vs.* Ag/Ag^+ (the solvent), slope; mV, Concn.; mM, supporting electrolyte; 0.1 M Et_4NClO_4. a) *vs.* SCE. b) The supporting electrolyte is reduced before the current reaches the limiting current. c) COS gives two waves in HMPA (see the text).

first wave height of CS_2. The number of electrons of COS reduction is regarded as unity, because the number of CO_2 reduction and of the first reduction step of CS_2 are both defined to be unity[2,6]. The slope from the wave analysis for CO_2 is 80–90 mV in most solvents, while that for COS changes from about 200 mV in AN to about 100 mV in large donor number solvents. The slope of the first wave of CS_2 changes from 60 mV to 100 mV. As for the second wave of CS_2, reversibility is generally well, but an accurate value can not be obtained owing to its small current.

COS gives two waves in HMPA in contrast to one wave in another solvent (shown in Fig. 10). The half-wave potentials of the first and second waves are −2.25 V and −2.74 V.

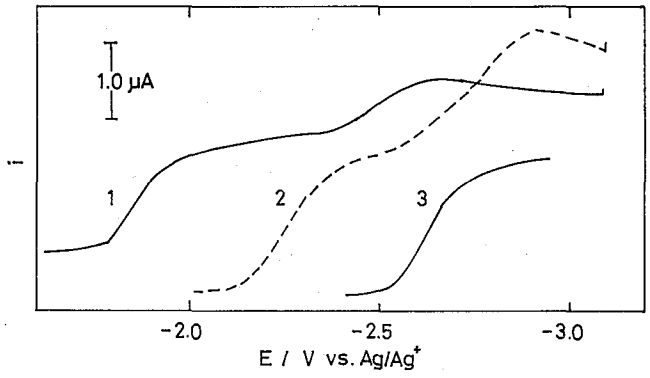

Fig. 10. D.c. polarograms of CS_2, COS, and CO_2 in HMPA containing 0.1 M Et_4NClO_4. (1) 1.0 mM of CS_2, (2) about 1.2 mM of COS, (3) about 1.1 mM of CO_2.

3-3 The Relation between the Donor Number and the Half-Wave Potential

The half-wave potential of CO_2, COS, and CS_2 expressed in the "rubidium scale"[13] is plotted against the donor number[14] of the solvent (shown in Fig. 11). The linearity is found between the donor number of the solvent and the half-wave potential of the wave of CO_2 and COS, and the first wave of CS_2. The half-wave

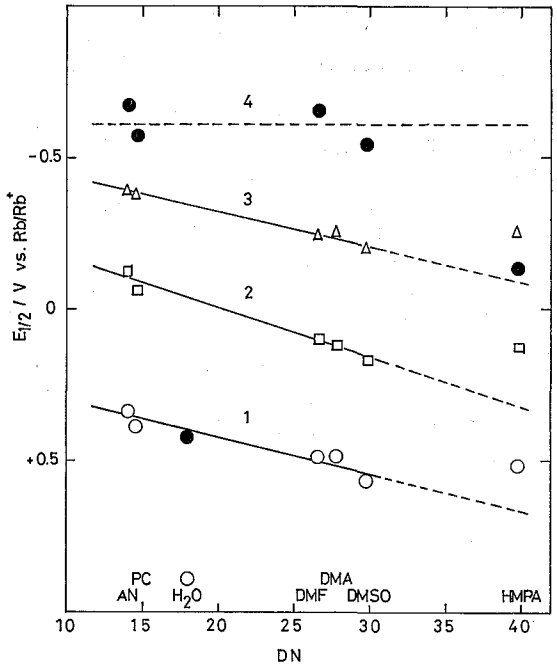

Fig. 11. The relation between half-wave potential of CO_2, COS, and CS_2 and the donor number of solvent (*vs.* the half-wave potential of Rb^+). (1) the first wave of CS_2, (2) the wave of COS, (3) the wave of CO_2, (4) the second wave of CS_2.

potentials shift toward positive potentials with the increase of donor number of the solvent. This tendency is contrary to that of metal ions; the half-wave potentials of some metal ions shift toward negative potentials with the increase of donor number of the solvent[15] because of the stabilization of the oxidant by the solvation.

The half-wave potential of COS changes somewhat more greatly with the change of donor number of solvent than those of CO_2 or CS_2, which corresponds to the fact that the reversibility of COS decreases remarkably with decreasing donor number of the solvents, as described previously.

In HMPA, the wave appears at a more negative potential than expected. This fact can be explained by supposing that the solvation to CS_2 also occurs to some extent owing to its strong basicity. According to Gutmann[15], bis-diphenylchrom (I) ion is considered as a better potential standard than rubidium ion. But even if the potential standard is converted to bisdiphenylchlom(I) ion, this tendency of positive shift due to the increase of donor number holds as well. It may be concluded that the solvation of an aprotic solvent to the oxidant (CO_2, COS, CS_2) is small and approximately same order to one another, but the solvation to the reductant (anion radical) increases with increasing of the donor number of solvent.

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